Chapter 5. Ouellette, 2/e. Chemistry X402.

Ch 5. Aromatic compounds.

This chapter follows closely on Ch 4 (alkenes), as it presents another type of unsaturated compound: aromatics, such as benzene. It is the last of three Ch (3-5) on "hydrocarbons".

Skip: Sect 7-11. These all deal further with reactions of aromatic compounds.

Also read: Sect 1.6, on resonance. That includes benzene as one example.

Practice quiz at web site: On use of the prefixes ortho etc.

Essay. Not assigned, but it is good biochemistry, dealing with how aromatic compounds, whether pollutants or drugs, may be metabolized by your body.

What is aromaticity? (levels of explanation)

The subject matter of this chapter is "aromatic compounds", yet it can be tricky to understand what that term means. Perhaps the most important point is that the term describes the behavior of certain chemicals: chemicals that appear to have double bonds, but do not act like it. The first structure that correlates with aromatic behavior is benzene. Understanding that in terms of a planar loop of 6 electrons in overlapping p orbitals gives some level of explanation, and lets us accommodate pyridine. But aromatic compounds need not have 6-membered rings, or even loops of 6 electrons. The theoretical basis of that is complex, but empirically it is embodied in Hückel's rule (p 140).

Fortunately, simply accepting that benzene is the characteristic aromatic compound is useful; most of the aromatic compounds we will encounter are accommodated within this idea (with some flexibility, to accept pyridine and naphthalene). Understanding the electron system of benzene is good, and is important if you are going on in organic chemistry. Doing this does require understanding the orbital description of bonding. We will consider this an "advanced" issue -- desirable, but not critical for our course.

You are not formally responsible for Hückel's rule (last subsection of Sect 5.2), or for the explanations of more complex aromatic compounds in Sect 5.3. However, you should recognize some of the compounds shown there as aromatic, even if you simply memorize them (naphthalene etc; pyridine etc). Fig 5.3 is helpful.

I have a web page on the nature of aromaticity. It is approximately equivalent to Ouellette's material. Again, you are not responsible for it, but may find it useful or interesting -- perhaps even fun, because of the pictures. (I wrote it for use with a previous book, which had no explanation at all of the nature of aromaticity, beyond "like benzene".)

The section on Computer Resources below includes an animation showing how aromaticity is explained in terms of the orbitals. It is similar to Fig 5.1.

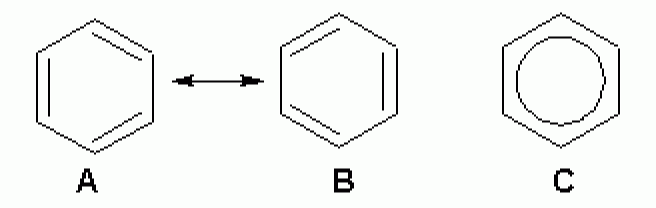
Other notes (and some "Pitfalls", marked with ⇒)

Sect 2. Resonance. Review Sect 1.6. Emphasize that the actual electron distribution is the average (or hybrid) of the ordinary-looking Lewis structures. The electrons do not move (resonate) between the various structures. Real bonds do not need to be single or double; in benzene the CC bonds are single-and-a-half.

> (Resonance is not restricted to organic compounds. For example, if you draw a Lewis structure for the phosphate ion, PO_4^{3-}, you could draw four equivalent structures; the actual structure is the resonance hybrid, with 3/4 of a charge on each O.)

Sect 2. Ouellette shows various ways of writing the benzene structure, but omits a very common one: a hexagon with a circle in the middle. The circle represents that π-ring (Fig 5.1).

> Parts A-B of the following figure show the two Kekulé structures, as resonance forms (p 140, middle). We often write only one of these to show a benzene ring. Structure C, with the circle in the hexagon, is another way to show benzene; it is equivalent to the A-B pair.



The disadvantage of using the circle is that it is hard to see how many bonds are on each C. So when bond number is important, use isolated bonds, but otherwise the circle is easy and common.

p 145, bottom. Ouellette shows several common names for aromatic compounds. **You should know**: toluene, phenol, aniline, benzaldehyde and benzoic acid. (Yes, that is somewhat arbitrary, but I think those are the most important ones.)

⇒ p 146, top. The prefixes ortho, meta & para can be used only for aromatic compounds with exactly two substituents. The practice quiz at the web site may help you with this, including the conditions required for using these prefixes.

⇒ p 146, bottom. The "group" based on benzene is called the phenyl group. Not only is it not benzyl, benzyl means something else. Also, be sure to distinguish these groups from the compounds benzene and phenol. See the "Phenyl group" page at the web site for a brief overview, with structures.

p 146, bottom. The phenyl group is often shown with its ring, but it is also common to abbreviate it, as C_6H_5-. The abbreviations Ph or ϕ (Greek letter phi) are also used.

> **You should also know** the nitro group -NO_2 (p 149) and the acetyl group (IUPAC: ethanoyl). I'm not sure where it is formally introduced, but the group attached to benzene in acetophenone (p 145 near bottom) is an acetyl group.

Sect 5. Top priority is to describe the main class of aromatic reactions, electrophilic substitutions, and to learn some common examples.

⇒ **Important**… Be sure to distinguish addition and substitution reactions. The ordinary English meaning of the words is relevant. A substitution reaction involves an exchange: AB + CD → AD + BC. [Yes, in that sense it looks similar to a double replacement reaction, from general chemistry. However, double replacement reactions involve ions, whereas the substitution reactions we discuss in organic chemistry involve covalent bonds.] The aromatic substitution reactions we discuss here involve only the hydrogens that are on the aromatic ring.

> You might want to look at parts of Sect 2.5. Be careful to not worry abut things there that have not yet come up. Also, he describes substitution a little differently than I do. You should accept both of our descriptions as essentially equivalent. Happy to discuss if not clear.

The material on mechanism of these reactions is "advanced".

pp 149-151, Friedel-Crafts. Part of this section is "advanced". At the bottom of p 149, he introduces the Friedel-Crafts alkylation, which you should know. In the rest of the section he discusses some complications and caveats of this reaction, and then goes on to some more reactions, which we do not need. For core coverage, you can stop this section at the end of p 149.

Sect 6. Advanced. Most important is to get a feel for the questions that are raised here: Substitutions on the ring affect subsequent substitutions, both in rate and position. If you look at the classification of substituents, Table 5.1, there are some obvious trends. Groups that are "strongly activating" (and o,p-directing) have a very electronegative atom on the ring. Groups that are "strongly deactivating" (and m-directing) have a very electronegative atom one position away from the ring, thus have an atom with a significant positive charge directly attached to the ring. I do not expect you to remember this table. Sect 5.7, which we skip, "explains" these effects.

Reaction summary. You are responsible only for #1-4. All of these are what type of reaction?

"Suggested" problems

For some basic problems on aromatic reactions, see my supplemental handout, attached.

Book: 11-22, 25-26, 33-40 (but some of those have some "advanced" aspects; emphasize the basic reactions). Others are "advanced", but may be good practice for you as open-book homework. For example, working through some of 1-10 would help you see that there is a logical basis for aromaticity, even if you are not responsible for remembering it. (If you tackle #23, see Errata note below.)

For written feedback, turn in a sampling of problems, especially some that challenged you.

Overview of skipped sections

Sect 7-8. Interpretation of rate effects; Interpretation of directing effects. As noted earlier, this section explains how one substituent affects subsequent substitutions. The ideas were introduced in Sect 6, which you should read. Those who are going on in organic chemistry might try Sect 7, but officially it is well beyond what we need here.

Sect 9. Reactions of side chains. Our main focus is reactions of the aromatic ring. This section discusses the effect of the ring on reactions of things attached to it. Those effects are significant for atoms directly attached to the ring.

Sect 10. Functional group modification. Direct aromatic substitution can only give you a few groups. But some of these can be converted to other groups.

Sect 11. Synthesis of substituted aromatic compounds. If you want to make an aromatic compound that has two substituents, what strategy should you follow? Does it matter which group you add first? These are the kinds of questions addressed here. Good organic chemistry.

Those who are going on in organic will find these skipped sections good introductions to material of great importance in organic (though of much less importance in basic biochem). You might find some of this easier after you have read more of the organic chapters, so you are familiar with more of the functional groups. If you want to try some of the exercises, from 29-, try to give reasons for each step and the order of steps. If you have trouble, turn in some, or let's discuss privately. Even doing a few of these could be a good preview of more advanced organic for you.

Errata

p 168, #17.
a. Either 1,2- or ortho- is fine. So long as there are exactly two groups on the aromatic ring, those position designators are equivalent.
b. Common name cumene is shown on p 145. Not important, but some students notice it.
c. And since we got started… this compound is mesitylene. I don't think it is in the book.

p 168, #23. Difficult! That it is o,p-directing is easy enough, since it does have lone pair electrons to offer. But S and C have the same electronegativity. S is bigger, and more polarizable. I would be surprised if it deactivates very much; I have not yet found another discussion of this. In contrast, the S in #24 lacks lone pairs and clearly carries a partial + charge; it will be strongly deactivating and m-directing.

p 169, #31. Answer is missing a CH_2 on side chain. That is, side chain should be propyl, with a Br in the 1 position of the side chain, next to the ring. With that in mind, explanation in terms of 2° C is weak. The better explanation is that the side chain position right next to aromatic ring is particularly reactive (resonance stabilization), as explained at the start of Sect 5.9. The "benzyl" intermediates are more stable than even 3°.

Further reading

W Mickelson et al, Packing C_{60} in boron nitride nanotubes. Science 300:467, 4/18/03. The C_{60} (fullerene) molecules are conducting and the BN walls are insulating, so we have a nanoscale insulated wire.

M Hara et al, Heterogeneous catalysis: a carbon material as a strong protonic acid. Angew Chem Int Ed 43:2955-2958, 5/24/04. Sulfuric acid is a major industrial chemical, with much of it used as a catalyst. A significant problem is that it is not easily recycled; a solid acid would be easier to handle for many purposes. The sulfonic acids of aromatics are of similar acid strength to H_2SO_4. Here they report progress toward making "a solid acid that is as active, stable, and inexpensive as sulfuric acid".

Y Saikawa et al, Pigment chemistry: The red sweat of the hippopotamus. Nature 429:363, 5/27/04. This work made the network news: hippos make their own sunscreen, which also has antibiotic properties. It is a Ch 5 (and 8) story, because the key functional groups are phenols and quinones (p 237). An interesting feature is the fairly high acidity of the phenol here, due to resonance stabilization of the anion. If you want to try this stuff, just wipe the face of a hot hippo -- so says the methods section of the paper.

E Stokstad, Toxicology: Factory study shows low levels of benzene reduce blood cell counts. Science 306:1665, 12/3/04. News. Benzene is known to cause leukemia. (Interestingly, toluene does not; this subtle difference appears to reflect the different ways the body metabolizes the compounds.) This new report suggests that chronic exposure to low levels of benzene (well below the levels considered relevant to leukemia) causes a reduction of the white cell count. The effects are small, and there was no evidence that the exposed people were sick; the importance -- and generality -- of this observation remain to be seen. The paper also talks about mutations that lead to increased susceptibility to benzene effects. There is an exchange of letters, discussing the merits of the conclusions, in Science 312:998, 5/19/06.

X Huang et al, Observation of d-orbital aromaticity. Angew Chem Int Ed 44:7251-4, 11/11/05. They show that the $Mo_3O_9^-$ ion (which includes a six-membered ring with alternating Mo and O) contains a d electron delocalized over the three (non-adjacent) metal atoms.

R C Kerber, If it's resonance, what is resonating? J Chem Educ 83:223, 2/06. A nice article about the awkward term we use to describe the novel features of benzene.

W B Jensen, The origins of the ortho-, meta-, and para prefixes in chemical nomenclature. J Chem Educ 83:356, 3/06. A couple of cautions… First, there are other uses of the terms than those for aromatic compounds. Second, the story does not reveal much "logic". From the "Ask the historian" column.

H-U Blaser, Chemistry: A golden boost to an old reaction. Science 313:312, 7/21/06. News. Ouellette talks about how aromatic amines can be made from nitro compounds (p 161). However, there can be complications if the molecule has other reducible groups. This news story discusses some developments in selective reduction.

J A Ellman, Chemistry: The direct approach. Science 316:1131, 5/25/07. News. Discussion of some new methodology for joining aromatic rings together.

D R Walt, Smells like bread. Nature Chemical Biology 3:306, 6/07. News. "Mammalian olfactory receptor genes have been engineered into a yeast expression system. The resulting cells provide a high-throughput screening system for studying receptor specificity and may find use as biosensors." One focus is using the system to detect DNT (dinitrotoluene). DNT is a marker for explosives; it is more volatile than the explosive TNT.

M Leslie, Plant biology: At long last, pathologists hear plants' cry for help. Science 318:31, 10/5/07. News. Plants use methyl salicylate (oil of wintergreen) to signal distress.

R Herges, Organic chemistry: Aromatics with a twist. Nature 450:36, 11/1/07. News. An aromatic Möbius strip? The two lobes of a p orbital are distinguishable; thus it is possible to imagine taking a π-electron ring, and twisting it -- like a Möbius strip. Turns out that Hückel's rule is now that 4n π electrons is the criterion for aromatic stabilization. This news article discusses work reporting a molecule whose conformation and therefore aromaticity varies with the polarity of the solvent. A cute story, but quite incomplete. The whole idea of aromatic Möbius strips dates back only to 2003, at least for any experimental support.

G Scalliet et al, Scent evolution in Chinese roses. PNAS 105:5927-5932, 4/15/08. The characteristic aromas of roses are dominated by, well, aromatic compounds -- in the Ch 5 sense. Among them are 2-phenylethanol and 3,5-dimethoxytoluene (DMT). Among wild roses, DMT is characteristic of Chinese roses; it is also common in modern roses. This paper explores how DMT is made, and how the enzymes needed for adding the two -OCH_3 groups likely evolved.

Y Zhou et al, Multifolded polymer solar cells on flexible substrates. Applied Physics Letters 93:033302, 7/21/08. Folding the solar cells, into a W shape, results in increased efficiency. The reflections within the folded structure allow more photons to be absorbed. The solar cells themselves use organic conducting polymers, some of them based on aromatic structures.

R E Maleczka, Jr., Chemistry: Copper puts arenes in a hard position. Science 323:1572, 3/20/09. News. Chapter 5 introduces the electrophilic substitution as a major reaction type with aromatics. It introduces the rules that guide substitution patterns, and the reasons for those rules. The work described here opens up a new path: under certain conditions, they achieve a preference for meta- substitution.

M Segal, Selling graphene by the ton. Nature Nanotechnology 4:612, 10/09. News feature. A graphene sheet is, simply, a layer of graphite -- a network of aromatic rings one atom thick. (In common usage, the term graphene is also used for small stacks of sheets.) One can think of a carbon nanotube as being a graphene sheet rolled up into a tube. Graphene and nanotubes share some interesting properties, such as two-dimensional electrical conductivity (in the aromatic plane), but graphene may be much cheaper to make. This news story discusses the developing market for graphene.

M J Rosseinsky & K Prassides, Materials science: Hydrocarbon superconductors. Nature 464:39, 3/4/10. News, about a new type of "high-temperature" semiconductor, in which the organic part is a hydrocarbon: no atoms other than C & H. It is an aromatic compound, with five fused rings (in a particular arrangement). An intriguing question is what will happen when a wider range of similar molecules are studied.

M. Saito et al, Dilithioplumbole: A lead-bearing aromatic cyclopentadienyl analog. Science 328:339, 4/16/10. If C does it, how about other members of the family? A common question. But there are important differences as you move down the group, including lower electronegativity (less than that of H, for all the elements below C), and larger size. Here they report a compound with a Pb in the ring, and they provide good evidence that the ring has aromatic character. This fits with occasional reports of aromatic compounds involving any of the group 14 elements.

Computer resources (See web page for details and links.)

Dr T Newton has an animation showing the bonding in benzene in terms of orbitals. In particular, note the loop formed by six p orbitals, one from each bonding C, overlapping sideways. This continuous loop of sideways-overlapping p orbitals, with six electrons, is responsible for the aromatic character. This item builds on Newton's item posted earlier for Chapter 4 on π bonding in alkenes. (This page also gives you more explanation of the basis of Hückel's rule, though the level is fairly difficult.) For a broader view of what aromaticity entails, see my page on this topic, listed below. (Newton's site is also listed on the web page for X402 Internet Resources, under General, as a broad resource for organic chemistry.)

Information about graphene.

The following pages from my web site were mentioned above:
- The "Phenyl group" page will help you with this and related terms. The page shows structures.
- The "Aromatic" page addresses the broader question, What does "aromatic" really mean? I encourage you to browse it, and enjoy the pictures!

Attached page: *Some extra problems on the basics of aromatic substitution reactions. You may want to do these before doing the book problems; mine are more basic.*

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